CLASSIFICATION ~~RESTRICTED~~

CENTRAL INTELLIGENCE AGENCY

INFORMATION ~~RESTRICTED~~

FOREIGN DOCUMENTS OR RADIO BROADCASTS

FDD FILE COPY

REPORT

CD NO.

COUNTRY	USSR
SUBJECT	Physics
HOW PUBLISHED	Monthly periodical
WHERE PUBLISHED	USSR
DATE PUBLISHED	February 1948
LANGUAGE	Russian

DATE OF INFORMATION 1947

DATE DIST. 26 Oct 1948

NO. OF PAGES 13

SUPPLEMENT TO

UNCLASSIFIED

FEB 2 1955 ~~us~~ /FDD

FOR OFFICIAL USE ONLY

THIS IS UNEVALUATED INFORMATION FOR THE RESEARCH USE OF TRAINED INTELLIGENCE ANALYSTS

THE NATURE OF THE CENTERS OF LUMINESCENCE IN

PHOTOCHEMICAL COLORED ALKALI-HALIDE CRYSTALS

M. L. Kats
Saratov State University
Submitted 4 June 1947

/Figures and table referred to herein are appended.7

The investigation of the luminescence of photochemical colored monocrystals of alkali-halide compounds, owing to the simplicity of their structure and the availability of detailed information on their optical and photoelectrical characteristics, is of great interest not only for the explanation of the mechanism of luminescence, but also for the understanding of photochemical processes in crystals.

Clear crystals of alkali-halide compounds, being naturally transparent in the visible and in the near ultraviolet parts of the spectrum, have very sharp and strong absorption bands in the relatively deeper ultraviolet part of the spectrum, the structure of which was accurately established in the research of Hilsch and Pohl [8].

With the absorption of light in the area of the natural absorption band and also under the influence of X-rays, color arises in alkali-halide crystals which causes the appearance of selective absorption in the so-called F-centers. Ultraviolet luminescence is found in these alkali-halide crystals containing F-centers. A good deal of research has already been devoted to this luminescence but the mechanism of the occurrence and the very nature of the centers of luminescence still remain unexplained. Even the opinion that the luminescence of photochemical colored alkali-halide crystals has dissociated F-centers does not have the proper experimental verification.

- 1 -

STATE	X	NAVY	X	NSRB		DISTRIBUTION							
ARMY	X	AIR	X	RDB	X	AEC	X						

STAT

Consequently, it is still not clear whether the luminescence of alkali-halide crystals is actually due to the creation of F-centers in the processes of photochemical coloring, or whether photochemical coloring only occurs simultaneously with the excitation of foreign atoms of random admixture, which naturally appears to be the actual cause of the luminescence of colored alkali-halide crystals similar to the activator admixtures of ordinary phosphorus.

The present work aims to explain this problem, which is very important for the understanding of luminescence and photochemical effects in colored crystals, by investigating the dependence of the ultraviolet luminescence of photochemical activated monocrystals of alkali-halide compounds on the concentrations of F-centers in the crystal.

After stopping the action of condensed Al-ray or X-ray excitation of photochemical colored alkali-halide crystals, four types of illumination are found: phosphorescence, illumination caused by visible light which we shall call a flash, thermal luminescence, and illumination caused by plastic deformation--or triboluminescence. In this work the dependence of luminescence on the concentration of F-centers for all types of illumination mentioned above is investigated.

The measurements were made by Kiropulos' method with the aid of a highly sensitive photon calculator with a platinum-sensitized photocathode on monocrystals of KCl and NaCl carefully cleansed of admixture, which occur in fusion.

Samples 1cc in size, spectrally colored by an undispersed light of the concentrated Al spark, were taken from large monocrystals. To measure the luminescence, the crystal was placed at a distance of 20 cm from the calculator. In front of the photocathode there was placed a diaphragm with an opening 0.4 cm in diameter to limit the light stream falling on the calculator. Since the light stream of the crystal luminescence was isotropic, then, by calculating the distance from the crystal to the calculator, which was sufficiently great compared with the dimensions of the crystal, we can, from the number of registered indications of photoelectrons, determine the total number of light quanta radiated by the crystal in all directions by using the formula

$$N = \frac{4 \pi R^2 N_0}{S \eta} \tag{1}$$

where N_0 is the number of registered indications of photoelectrons, R is the distance of the crystal from the calculator, S is area of the aperture in the diaphragm (acting on the surface of the photocathode), η is the electron emission from the platinum photocathode in the spectral region of the luminescence of NaCl and KCl, and N is the total number of light quanta radiated by the crystal.

The concentration of F-centers is determined by the formula as presented by Mollwo and Ross [2]:

$$N_F = 1.31 \times 10^{17} \frac{n_0}{(n_0 + 2)^2} K H = A_R H \tag{2}$$

Here n_0 is the refraction index of the colored crystal in the maximum absorption area in the visible part of the spectrum, K is the coefficient of absorption in the maximum F-absorption band, expressed by the inverse of the centimeters, H is the half-width of this band in electron-volts, and A is a constant with the following numerical values for NaCl and KCl: $A = 1.04 \times 10^{16} (cm^2 \cdot eV)^{-1}$ and $A = 1.1 \times 10^{16} (cm^2 \cdot eV)^{-1}$.

The measurement of the absorption coefficient, K, and the half-width of the absorption band, H, is computed with the aid of a double mono-chromator with glass optics and an antimony-cesium photoelement. The computing device has a light source of low intensity. It measures the absorption coefficient of weakly colored crystals and does not bring

- 2 -

STAT

forth any noticeable decoloration. The schematic layout of the instruments is shown in Figure 1.

The Flash

Through the action of the visible light in the absorption area of the F-band, the colored crystal of an alkali-halide compound may be decolorized. Moreover, the crystal radiates in the ultraviolet region. The author first measured spectrums of phosphorescence and the flashes which were obtained from colored NaCl crystals /3 7 with the aid of a quartz monochromator.

It appeared that the spectrum of the flash and the phosphorescent part, devoid of the inner intensity of the NaCl crystals in the spectral sensitivity area of the photon calculator with the sensitized platinum photocathode (from 2,000 to 3,200 Å), consisted of one band with the maximum λ near 235 $m\mu$. (Only in deformed samples and in certain samples of monocrystals of NaCl is there still found one band with the maximum λ near 290 $m\mu$, which was found by the author in 1936 /3 7 and ascribed to the transfer of electrons with F-levels on the so-called U-level. The latter, as was shown later, shows the presence of admixtures of foreign atoms.) Subsequent and more exact measurements with the aid of a double-dispersion quartz monochromator have shown that the maximum λ of this band is found near 240 $m\mu$ (5.14 eV) and its half-width is equal to 0.47 eV.

The light spectrum of KCl crystals in the range 2,000-3,200 Å also consists of one band with the maximum λ near 270 $m\mu$ and a half-width of 0.46 eV.

Podashevskiy and Polonskiy / 4 7 repeated our measurements with the aid of a quartz monochromator and photon calculator on X-rayed crystals of NaCl. They also established that the spectra of phosphorescence and flashes of these crystals are alike and consist of one band with the maximum λ near 248 $m\mu$ (~5eV). The difference of 8 $m\mu$ in the maximum from our measurements is not important when the experimental difficulties of measuring such weak light currents, as the illumination of alkali-halide crystals appear to be, at the relatively wide spectral bands of light is considered. Similar results were obtained by Kudryavtsev /3 7.

In this work, the investigation of samples of crystals of NaCl and KCl also brought similar spectrums of flashes and phosphorescence with the maximum λ of the band near 240 $m\mu$ (NaCl) and 270 $m\mu$ (KCl).

The measurement of the dependence of total luminescence on the concentration of F-centers was carried out by the method mentioned above. It was established that the number of quanta radiated by the crystal under the action of the visible light until complete decolorization was proportional to the concentration of F-centers in the crystal (Figure 2).

With the change of the absorption coefficient k from 10^{-2} mm^{-1} to 14×10^{-2} mm^{-1}, which corresponds to changes of the concentration from 5×10^{14} to 0.7×10^{16} of F-centers in 1cc (KCl), this dependence can be expressed by the formula

$$N = r\, N_F = r\, A\, k\, H \tag{3}$$

where γ is the coefficient of illumination, determined from the curves in Figure 2. It is equal to 1.44×10^{-2} for NaCl. It follows from this that out of 100 destroying actions of visible light of F-centers, on the average, 1-1.5 /F-centers/ disassociate with the radiation of light quanta in the ultraviolet ray.

- 3 -

STAT

RESTRICTED

Phosphorescence

After stopping the excitation action of the condensed Al-spark, the crystal phosphoresces under the ultraviolet ray. The dependence of the number of light quanta radiated by the phosphorescent crystal can be expressed by formula (3), but with other numerical values of the illumination coefficient γ , which for phosphorescence is 1.04×10^{-3} for KCl and 6.2×10^{-4} for NaCl, i.e., 14-15 times less than for the flash.

Unlike the case of flash illumination the crystal, after the phosphorescence has practically faded, is not completely decolored, and momentary illumination by visible light brings repeated phosphorescence. This process of momentary illumination by the action of visible light can be repeated many times until the complete decoloration of the crystal, but the integral light sum does not exceed, with a given concentration of F-centers, the number of quanta radiated by the crystal under the continuous action of visible light until the complete decoloration of the crystal.

Thermoluminescence

The heating of a colored crystal to 150-200°C brings about complete decoloration which accompanies thermoluminescence under ultraviolet rays, with a spectral band similar to phosphorescence and flash [5]. The dependence of the total light on the concentration of F-centers in the crystal is also not determinable in this study, but the coefficient of illumination under thermoluminescence, characterized by the probability of the dissociation of F-centers with radiation is almost twice the coefficient of illumination of the flash, which now becomes 2.13×10^{-2} for NaCl and 1.65×10^{-2} for KCl.

Illumination Caused by Plastic Deformation

Under the influence of plastic deformation, photochemical colored alkali-halide crystals also luminesce under ultraviolet rays, with a spectral band similar to the thermoluminescence band. The energy radiated by the crystal under the influence of plastic deformation depends on the concentration of F-centers as well as the strain under which the crystal is placed.

From the curves of Figure 3, it is obvious that for a given concentration which differs for various amounts of strain, a region occurs in which the total light is independent of the absorption coefficients. The greater the strain the higher the concentration at which this region occurs, and only at strains which bring about the full decoloration of the crystal will the light sum radiated by the crystal be proportional to the concentration of the F-centers. The average value of the coefficient of illumination in plastic deformation is $\gamma = 1.41 \times 10^{-5}$ (Table 1).

If the concentration of F-centers and the energy of deformation of the crystal are known, then by using the formula

$$ W = N_F \, \Delta W = \tfrac{1}{2} \, \sigma \, p^2 \, V, \qquad (4) $$

the activation energy that is necessary for the dissociation of the F-centers can be computed. In formula (4), W is the energy of deformation, C is elasticity of coefficient of the crystal, P is the decoloration strain, N_F is the number of F-centers, V is the size of the crystal, and ΔW is the activation energy which by our measurements is 4×10^{-13} ergs (Table 1),

- 4 -

RESTRICTED

STAT

instead of the smaller value of 1.83×10^{-14} ergs. Obviously the difference is explained in that in Fedenev's work the F-centers were not measured and were estimated arbitrarily by the intensity of the color.

The Mechanism of Illumination

In the earlier suggested quantum-mechanic models [7] for the explanation of the coloration processes and the inherent photoeffect in colored alkali-halide crystals, certain very important peculiarities which are found in the proper absorption bands of pure alkali-halide crystals were not studied. The latter, as is known, does not have a sharp border in the long-wave portion but, falling slowly, stretches out far into the long-wave part of the spectrum. Hilsch and Pohl [8], for example, succeeded in tracing the effect of the drop in the long-wave curve of natural absorption on the center of coloration down to the visible part of the spectrum.

In photochemical coloration of alkali-halide crystals, a light in the region of the drop in the long wave of the natural absorption is usually used. In the coloration of a crystal of KBr, the maximum absorption of which lies near 1875 Å, Smakula used a monochromatic light in a long-wave region (203 and 199 mμ). It was shown that this appears to be an arrangement necessary to satisfy the coloration. According to his data on concentration of F-centers at saturation, it is smaller the closer the excitation wave length gets to the maximum natural absorption band.

Investigations along the mechanical, thermal, optical and electrical effects in the absorption of alkali-halide crystals show that the long-wave slope of natural absorption is dependent on the crystal structure defects and would be absent in a crystal of ideal structure. As for the influence of the dislocation of the crystal structure on the long-wave slope, it is obviously indicated that the intensive formation of F-centers does not decrease the absorption coefficient in the long-wave slope of the absorption curve, which is made even more clear, and that the absorption coefficient in this part of the curve increases [10].

In the diagram of the energy levels (Figure 4), the absorption in the long-wave slope in the curve of natural absorption corresponds to the system of local levels, L, distributed close to the upper edge of the zone filled with the energy levels, A.

These local levels in uncolored crystals are normally filled with electrons. The absorption of light in the maximum or long-wave slope of the curve of the natural absorption (passages a and b in Figure 4) is due to the transfer of an electron in the conductivity zone, B, and with the creation of a positive hole in zone A, or on the L-level. If the hole is formed in the absorption in zone A, then it fills with electrons from the local L-level and is thus localized just as in the case of the absorption in long-wave slope on one of the local L-levels.

Part of the electrons, falling into the conductivity zone, return to the original state and recombine with the positive holes. They are finally localized on the local F-levels which are found below the conductivity zone at 2.63 eV in NaCl and 2.19 eV in KCl, depending on the so-called F-centers. Thus the localization of the electron and the hole occurs in different places of the crystal, and this explains the formation of stable coloring.

Study of local L-levels in absorption and coloration processes was not considered in earlier diagrams for the levels of alkali-halide crystals [7], and because of this, the formation of stable coloring along these lines had not been thought of.

- 5 -

In regard to the nature of F-centers two hypotheses exist. According to Frankel's [11], Pohl's [1], and Hippel's [12] models, F-centers are represented as ions of alkali metal which are caught by electrons and made into quasi-neutral atoms of alkali metal.

According to Mott's [13] and deBur's hypotheses, F-centers are represented as electrons, localized in places where there are no negative halide ions. Such F-centers will be called nonatomic F-centers to distinguish them from the atomic.

The localized state of the electron, also identified with F-centers [14], can, according to Landau [15], occur as a result of the deformation brought about by the photoelectrons themselves even though there is no structural defect in the crystal.

All indicated processes of the electron capture appear possible. But the probability of their realization and also the stability of the created F-centers will obviously vary with various methods of the electron capture. The least stable, probably, will be the F-centers appearing as electrons which are localized in places where there are no negative halide ions. In the presence of positive holes in zone A, these electrons will descend, recombining with the holes and emitting light quanta (3.14 eV for NaCl and 4.57 eV for KCl).

Thus, phosphorescence of colored alkali-halide crystals (passage d on Figure 4) is dependent on the recombination of the electrons, found in places where there are no negative halide ions, with positive holes in zone A. The latter arise due to the thermal change of the electron from the basic zone to the vacant places of the levels (passage c in Figure 4). The probability of filling the local L-level with electrons from the basic band should increase exponentially with the temperature

$$\alpha = \alpha_0 \, e^{-w/kT} \tag{5}$$

where W is the difference of the energy between the upper edge of zone A and the local L-level.

Since the time of interruption of the positive hole in zone A is very short in comparison with continuous interruption of the hole on the local L-level, then the extent of phosphorescence will be determined by the velocity of the thermal change of the electrons from zone A to the local L-level. If the latter is found at a similar distance from zone A, then at constant temperature we have

$$dn/dt = -\alpha n \tag{6}$$

where n is the number of positive holes on the local L-level. Integrating equation (6) and making $n = n_0$ at $t = 0$ we get

$$n = n_0 \, e^{-\alpha t} \tag{7}$$

and the intensity of the illumination

$$I = k \frac{dn}{dt} = k \, \alpha \, n_0 e^{-\alpha t} \tag{8}$$

which corresponds to that obtained earlier by the author and other inves-

- 6 -

RESTRICTED

tigators [4, 16] by experimental data, according to which the attenuation
of the ultraviolet phosphorescence of photochemical colored crystals of
NaCl and KCl appears according to exponential laws.

The activating actions of visible light coincide with the transposition
of electrons through a conductivity zone from one F-level with little
probability of recombination (atomic F-centers) to other F-levels with a
greater probability of recombination (nonatomic F-centers). With an
uninterrupted action of visible light (flash) the electrons in the non-
atomic F-centers are constantly lost and replenished, depending on the
illumination of the crystal, the crystal is decolored faster, and the
greater the intensity of the flash the greater the intensity of the phospho-
rescence. However, the spectrums of the flash and phosphrescence are
similar since the changes of the electrons are accomplished within one and
the same level. This conclusion is found to be in complete accord with
experimental data.

Since the light sum, radiated by the crystal at simultaneous phospho-
rescence, is noticeably smaller than the total number of light quanta
radiated by the crystal under the influence of visible light to complete
decoloration, then it follows that the number of nonatomic F-centers is
markedly smaller than the atomic F-centers, i.e., the probability of the
formation of nonatomic F-centers is noticeably less than the probability
of the formation of atomic F-centers. If we consider that every electron
producing nonatomic F-centers changes into the original state with the
radiation of light quanta, then, from the values of the illumination co-
efficients, it follows that the nonatomic centers make up only 0.17% for
KCl and 0.67% for NaCl of the number of F-centers of all types. This
relationship remains constant and does not depend on the concentration of
the other F-centers.

The very small relative concentration of the nonatomic F-centers is
explained by the small concentration space in which halide ions are
absent in comparison with the concentration of ions of the alkali metal
to which the electrons can combine to form atomic F-centers.

In thermoluminescence, the replenishing of nonatomic F-centers occurs
as a consequence of diffusion, at which the electrons forming the atomic
F-centers skip from one group of ions of alkaline metal to others, forming
an effective movement of F-centers. A similar movement of F-centers is
accomplished faster through a conductivity zone due to the tunneling effect
without the transfer of electrons. This explains why the illumination
coefficient of thermoluminescence is greater than the illumination
coefficient of the flash, or in the latter case why a significant part of
the electrons, spattering the light in zone B, goes to zone A without any
registered radiation. (If the changes are accompanied by radiation, then,
as can be ascertained from the diagram of the levels (Figure 4), it should
lie below 2,000 Å. i.e., beyond the limits of transparency of the quartz
tube of the photon calculator.)

The mechanism of luminescence under the influence of plastic deformation
is obviously similar to the mechanism of thermoluminescence with the
difference that the activation energy is transmitted by the electrons due
to the deformation energy of the crystal.

We must notice that, from the examined quantum-mechanic model, the
additive colored alkali-halide crystal in which F-centers are formed by
electrons introduced into the crystal externally should not luminesce,

- 7 -

RESTRICTED

RESTRICTED

STAT

which agree with the findings of D'yachenko /16/. In such crystals the local L-levels are filled up with electrons, and only after their activation by X-rays or by light from the area of the natural absorption band can luminescence be found.

Thus, our findings in this work, on the dependence of the luminescence of photochemical colored alkali-halide crystals on the concentration of F-centers and on the association with earlier data of the light spectrum, and on the spectral dissociation of stimulated action of visible light, fully verify that ultraviolet luminescence of colored alkali-halide crystals and the formation of F-centers is dependent not on the random occurrence of foreign atoms, but on the characteristics of a clear crystal, arising in the process of thermal and optical dissociation of F-centers.

BIBLIOGRAPHY

(1)   R. Pohl, _Proc. Phys. Soc._, 49, extrapart, 3, 1937

(2)   E. Mollwo and W. Ross, _Gott. Nachr._ 1, 107, 1938

(3)   V. M. Khdir sev, _ZHETF_, 4, 709, 1934
      M. L. Kats,   ture, 138, 833, 1936; _Sov. Phys._, 4, 373, 1937; _ZHETF_, 8, 100, 1938
      N. N. Fedenev, _ZHETF_, 8, 404, 1938
      M. N. D'yachenko, _ZHETF_, 8, 105, 1938

(4)   Podashevskiy and Polonskiy, _DAN SSSR_, 21, 15, 1938

(5)   M. L. Kats, _DANSSSR_, 30, 781, 1941

(6)   N. N. Fedenev, _ZHETF_, 10, 470, 1940

(7)   P. S. Tartakovskiy, _ZHETF_, 4, 215, 1934

(8)   R. Hilsch and R. W Pohl, _ZS f Phys._, 68, 721, 1931

(9)   A. Smakula, _ZS f Phys._, 63, 762, 1930

(10) E. Rexer, _Phys. ZS_, 36, 602, 1935

(11) Ya. Frenkel, _Sov. Phys._, 5, 911, 1934

(12) A. Hippel, _Jour. Apple. Phys._, 8, 815, 1937

(13) Mott, _Prox. Phys. Soc._, 49, extrapart, 3, 1937

(14) D. I. Blokhintsev, _ZHETF_, 6, 1093, 1936

(15) L. Landau, _Sov. Phys._, 3, 664, 1933

(16) N. D'yachenko, _ZHETF_, 17, 134, 1947

/Appended figures, table follow._7

- 8 -

STAT

Figure 1
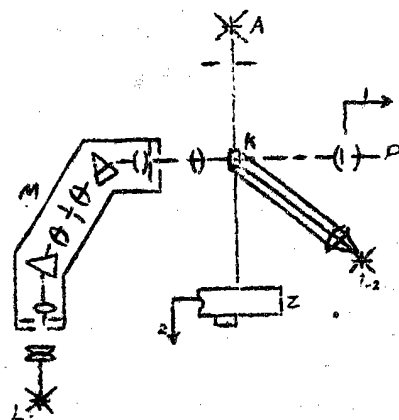
M   -   Monochromator

X   -   Crystal

Z   -   Photon Calculator

L_1 -   Source of Light for Measuring the Absorption (an Incandescent Lamp 12-v, 25-w)

A   -   Source of Excitation (Condensed Spark or X-Ray Tube)

P   -   Photoelement

L_2 -   Source of Light for the Decoloration of the Crystal (1,000-w Projection Lamp)

1 and 2   -   To Amplifiers

- 9 -

STAT

RESTRICTED

Table 1.

The effect of plastic deformation on ultraviolet luminescence of a photochemical colored crystal of NaCl (the deforming pressure is applied at the moment the excitation is stopped).

| Coefficient of Absorption $k(mm^{-1})$	Number of F-centers (per cc)	Decolor- izing Pressure (g/mm^2)	Total Number of Quanta Radiated by the Crystal		Energy used in the Annihilation of One F-Center W (erg)
1.2×10^{-2}	0.59×10^{15}	57	0.75×10^{12}	1.28×10^{-3}	4×10^{-13}
2×10^{-2}	0.98×10^{15}	95	0.12×10^{12}	1.26×10^{-3}	4×10^{-13}
3.4×10^{-2}	1.66×10^{15}	130	2.4×10^{12}	1.45×10^{-3}	4.2×10^{-13}
5.7×10^{-2}	2.79×10^{15}	160	3.85×10^{12}	1.38×10^{-3}	3.6×10^{-13}
8×10^{-2}	3.9×10^{15}	200	5.69×10^{12}	1.46×10^{-3}	4×10^{-13}
10.3×10^{-2}	5×10^{15}	220	7.45×10^{12}	1.49×10^{-3}	3.9×10^{-13}
12×10^{-2}	5.48×10^{15}	236	7.89×10^{12}	1.44×10^{-3}	4×10^{-13}
14.2×10^{-2}	6.9×10^{15}	265	10.42×10^{12}	1.51×10^{-3}	4.1×10^{-13}

RESTRICTED
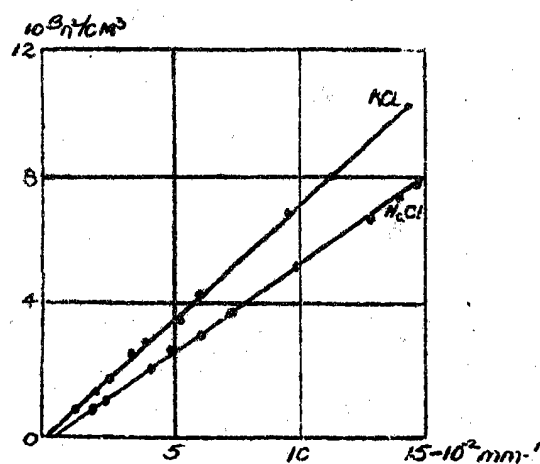
Figure 2

The number of quanta radiated by a photochemical colored crystal at complete decoloration due to the action of visible light as a function of the absorption coefficient at the F-band maximum.

Figure 3
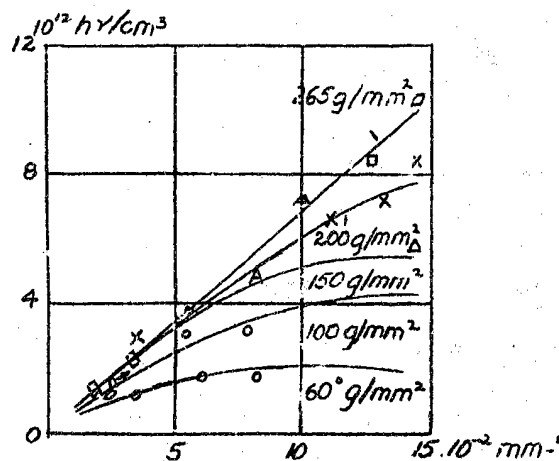
Total luminescent light from a photochemical colored crystal of NaCl under plastic deformation at a constant pressure as a function of the absorption coefficient $\mathcal{E}$ at the F-band maximum.

- 12 -

STAT

Figure 4

Diagram of the Absorption and Luminescence Processes for NaCl and KCl Crystals

- E N D -